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METHOD OF ACID PICKLING OF CR-CONTAINING STEEL PLATE
[C r 含有鋼板の酸洗法]

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SPECIFICATION

1. Title of the Invention

METHOD OF ACID PICKLING OF CR-CONTAINING STEEL PLATE

2. Scope of Patent Claims:

(Claim 1) A method of acid pickling of a Cr-containing steel plate, characterized in that a Cr-containing steel plate, which is coated with an oxide film, is electrolytically pickled by a pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein one type or two or more types of nitrate salt, sulfate salt, fluorosilicate salt and fluoroborate salt are mixed.

3. Detailed Description of the Invention

[Technical Application Field of the Invention]

The present invention relates to a method of acid pickling of a Cr-containing steel plate such as an alloy steel plate containing a small amount of Cr, austenite group steel plate, ferrite group steel plate, martensite steel plate and stainless steel plate.

[Prior Art]

The oxide film, which is generated on the surface of a steel plate containing a small amount of Cr, which has heat history

¹ Numbers in the margin display pagination in the foreign text.

of hot rolling or heat stretching/annealing, or a Cr-alloy steel plate, which is annealed after being cold-rolled, causes many problems such as damaging of the flat and smooth surface of the finished product and shortening of the life of the dice, which is used during the spinning process. Therefore, it is necessary to completely remove said oxide film. To achieve this purpose, various types of acid pickling solutions are used. For example, as examples of the above described acid pickling solutions, "Steel Handbook by Maruzen KK, page 1258, table 15.3 (April 5, 1962)" discloses a solution of nitric acid and boric acid, solution of sulfuric acid, boric acid and chromic acid and solution of sulfuric acid, nitric acid and boric acid. In addition, Japanese unexamined published application No. Sho 56-81688 discloses a sulfuric acid solution and a mixed solution of ferric sulfate and sulfuric acid as the acid pickling solutions.

[Problem to be Solved by the Invention]

By using one of the above described acid pickling solutions, it is possible to effectively perform the acid pickling in the dipping process. To complete the acid pickling in a shorter period, it is necessary to use the electrolytic method. If the above described acid pickling solution is used, it is possible to remove the oxide film in a relatively short period and the finished surface has a fairly good appearance. However, the rate

of deterioration of the performance of the solution is significantly fast and the cost of the acid pickling is increased. Especially, when the acid pickling solution, which is mainly made from nitric acid and boric acid, is used in a long acid pickling/dipping process, the finished surface of the steel plate tends to significantly deteriorate.

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As another method of removing the oxide film, it is possible to use the method wherein the oxide film is electrolyzed in a neutral salt aqueous solution such as sulfate of soda. In this case, however, iron in the steel plate is rarely dissolved and, although the finished surface is macroscopically good, microscopic oxide films tend to remain, or the Cr-deficient debris remains thereby deteriorating the corrosion resistance. Therefore, it is necessary to apply the method for a long period of time.

In addition, as the method of treating salt, it is possible to use the method wherein the oxide film is treated in mixed molten salt of caustic soda, caustic potash and nitrate of soda and then electrolyzed in a nitrate aqueous solution. However, the cost of this method is high.

The objective of the present invention is to solve the above described problems of the conventional acid pickling technologies and provide the method of acid pickling of a

Cr-containing steel plate, wherein the steel plate with a good finished surface can be obtained by a short-period electrolytic treatment.

[Means Used to Solve the Problem]

The present invention solves the problems of the method of acid pickling of a Cr-containing steel plate by electrolytic pickling the Cr-containing steel plate, which is coated with an oxide film, in a pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein one type or two or more types of nitrate salt, sulfate salt, fluorosilicate salt and fluoroborate salt are mixed.

[Operation]

Next, the detail of the present invention will be described.

A steel plate containing a small amount of Cr, which has heat history of hot rolling or heat stretching/annealing, or a Cr-containing steel plate such as a stainless steel plate, that is, the steel plate wherein an oxide film with a large thickness, which damages various practical properties, is coated on the surface, is electrolytically pickled in an acid pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein one type or two or more types of nitrate salt, sulfate salt, fluorosilicate salt and fluoroborate salt, which

are the acid pickling speed promoting agents, are selectively mixed.

According to the present invention, sulfuric acid, which is used as the base compound, is added to the solution so as to increase the lytic action and conductivity of the oxide film. When sulfuric acid is used together with other solvents, which are used in the present invention, if its concentration is less than 20 g/l, the acid pickling efficiency is significantly decreased. If the concentration of sulfuric acid is more than 400 g/l, the acid pickling is excessive thereby damaging the surface and thus the external appearance. Therefore, according to the present invention, sulfuric acid is used at the concentration of 20 to 400 g/l. In addition, nitrate salt, which is selectively mixed in the solution, not only improves the speed of removing the oxide film, but also has the effect of inhibiting the excessive acid pickling of the base. Although sodium nitrate is most commonly used as nitrate salt, any nitrate salt such as potassium nitrate and ammonium nitrate can be effectively used.

Sulfate salt such as sodium sulfate has the effect of inhibiting the excessive electrolytic acid pickling. This effect is especially conspicuous in the Cr-alloy steel plate, which contains a relatively small amount of Cr.

Fluorosilicate salt such as fluorosilicate of soda and potassium fluorosilicate and fluoroborate salt such as

fluoroborate of soda and ammonium fluoroborate can significantly increase the speed of removing the oxide film.

Various types of the above described additives must be selectively used depending on the type of the subject steel and the thickness of the oxide film, which is determined by the manufacturing process. Basically, as the content of Cr is increased, the temperature, to which the steel is exposed during the manufacturing process, is increased and the period of the treatment is increased, the number and concentration of the additives are increased.

As for the polarity of the electrolytic acid pickling, according to the present invention, normally, the steel plate is used as the anode. Depending on the type of the steel and the intended-end usage, first the cathode is acid pickled for a short period and subsequently the anode is acid pickled. The order of acid pickling is discretionally selected. In addition, when the thickness of the oxide film is extremely large or the oxide film must be removed in a significantly short period, a mechanical treatment such as the pre-acid pickling skin pass process, repeated bending process and shot blasting process can facilitate removal of the oxide film.

[Working Examples]

Next, the working examples of the present invention will be described.

[Working Example 1]

430-group, 410-group and 409-group stainless steel plates and cold-rolled 7 % Cr-containing steel plates were annealed in a continuous annealing line thereby removing the oxide films under the acid pickling conditions shown in Table 1. As shown in Table 1, the Cr-containing steel plates, which were acid pickled under the conditions of the present invention, had excellent performance in the external appearance, contact resistance and corrosion resistance, which matched that of the conventional method, which requires the long-period treatment.

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Table 1: Working Examples of the present invention: No. 1

Test No.	Subject	Original plate	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)
			H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆			
1	Not the method of the present invention	A								Anode: 10
2	Method of the present invention	A								Anode: 7
3	Method of the present invention	C								Anode: 6
4	Method of the present invention	A								Anode: 6
5	Method of the present invention	B								Anode: 5
6	Method of the present invention	C								Anode: 3
7	Method of the present invention	A								Anode: 5
8	Method of the present invention	A								Anode: 5
9	Method of the present invention	D								Anode: 7
10	Method of the present invention	A								Anode: 10
11	Method of the present invention	A								Anode: 5
12	Method of the present invention	B								Anode: 5

13	Method of the present invention	C							Anode: 5
14	Not the method of the present invention	A							Anode: 5
15	Method of the present invention	A							Anode: 5
16	Method of the present invention	B							Anode: 5
17	Method of the present invention	C Especially large thickness of the oxide film							Anode: 5
18	Method of the present invention	A							Anode: 5
19	Method of the present invention	Same as above							Anode: 5
20	Method of the present invention	A							Cathode → Anode: 4
21	Not the method of the present invention	C							Anode: 5
22	Comparative method	A	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 50 seconds
23	Comparative method	B	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 40 seconds
24	Comparative method	C	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 40 seconds

25	Comparative method	A	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 70 seconds
26	Comparative method	B	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 60 seconds
27	Comparative method	C	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 60 seconds

A: 430-group

B: 410-group

C: 409-group

D: 7 % Cr-containing steel

(All were the annealed material with a plate thickness of 1.0 mm)

Cathode: cathode electrolysis

Anode: anode electrolysis

[Translator's note: numbers are omitted.]

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Table 1: Working Examples of the present invention: No. 1 (continued from above)

Test No.	External appearance		Contact resistance (mΩ)	Corrosion resistance*	Remark
	Visual evaluation	GDS*			
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14	Excessive acid				

	pickling				
15					
16					
17					After the 0.5 % skin pass, acid pickling
18					After the shot blasting, acid pickling
19					
20					
21					
22					
23					
24					
25					
26					
27					

*: Measurement of the oxide film by glow discharge. *: SST 96llrs pursuant to JIS Z-2371

1: <--> 10:
Complete removal of the oxide film Non-acid pickling state

@: <--> X:

Good Poor

[Translator's note: numbers and marks (@, ^ & X) are omitted.]

[Working Example 2]

In addition, the method of the present invention can be effectively used to remove the oxide film, which has an extremely large thickness, from the Cr alloy steel plate such a hot-rolled plate. The method of the present invention can be used singly or in combination with the conventional dipping acid pickling method. Table 2 shows examples of removal of the oxide films.

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Table 2: Working Examples of the present invention: No. 2

No.	Original plate (hot-rolled plate)	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)	Oxide film removal rate (%)	Remark
		H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆					
i	A										
ii	B										
iii	C										
iv	D								90 seconds dipping		Comparative Example
v	E										

A: 430-group

B: 410-group

C: 409-group

*Measurement by GDS

[Translator's note: numbers are omitted.]

[Working Example 3]

In addition, the method of the present invention is effective in removing the oxide film from the Cr-containing steel plate, which is annealed at 800 to 1,000 °C for 1 minute after being hot-rolled. The method of the present invention can be used singly or in combination with the conventional dipping acid pickling method. Table 3 shows examples of removal of the oxide films.

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Table 3: Working Examples of the present invention: No. 3

No.	Original plate (hot-rolled and annealed plate)	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)	Oxide film removal rate (%)	Remark
		H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆					
I	A										
II	B										
III	C										
IV	D								120 seconds dipping		Comparative Example
V	E										

A: 430-group

B: 410-group

C: 409-group

*Measurement by GDS

[Translator's note: numbers are omitted.]

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[Effect of the Invention]

As is described above, the present invention provides the method of rapidly acid pickling the oxide film, which can decrease the cost of the high-speed mass production of the Cr-containing steel plates. The method of the present invention is excellent in economic efficiency and prevention of pollution and has a significantly high industrial value.

Amendment

August 3, 1985

To: Mr. Michiro Uga, Commissioner of Patents

1. Disclosure of the Case

Japanese Patent Application No. Sho 60-115274

2. Title of the Invention

Method of Acid Pickling of Cr-containing Steel Plate

3. Party who makes the Amendment

Relationship with the case: Patent Applicant
Address: 2-6-3 Ohtemachi, Chiyoda-ku, Tokyo
Name: (665) Nippon Steel Co., Ltd.
Representative: Yutaka, Takeda

3. Agent

Address: T105, 8th Floor, Mori Building No. 1, 1-12-1
Nishi-shinbashi, Minato-ku, Tokyo, Tel: (503)4877
Name: Patent Attorney (6496): Yasushi, Yoshijima

4. Date of Amendment Directive

Voluntary

6. Subject of the Amendment

"What is Claimed:" of the specification, "Detailed Description of the Invention"

7. Content of the Amendment

(1) "What is Claimed is:" is amended as follows:

"A method of acid pickling of a Cr-containing steel plate, characterized in that a Cr-containing steel plate, which is coated with an oxide film, is electrolytically pickled in a pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein one type or two or more types of nitrate salt, sulfate salt, fluorosilicate salt and fluoroborate salt are mixed."

(2) Table 1 of pages 7 and 8 of the specification is amended as the Attachment.

Table 1: Working Examples of the present invention: No. 1

Test No.	Subject	Original plate	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)
			H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆			
1	Not the method of the present invention	A								Anode: 10
2	Method of the present invention	A								Anode: 7
3	Method of the present invention	C								Anode: 6
4	Method of the present invention	A								Anode: 6
5	Method of the present invention	B								Anode: 5
6	Method of the present invention	C								Anode: 3
7	Method of the present invention	A								Anode: 5
8	Method of the present invention	A								Anode: 5
9	Method of the present invention	D								Anode: 7
10	Method of the present invention	A								Anode: 10
11	Method of the present invention	A								Anode: 5
12	Method of the present invention	B								Anode: 5

13	Method of the present invention	C							Anode: 5
14	Not the method of the present invention	A							Anode: 5
15	Method of the present invention	A							Anode: 5
16	Method of the present invention	B							Anode: 5
17	Method of the present invention	C							Anode: 5
18	Method of the present invention	A (Especially large thickness of the oxide film)							Anode: 5
19	Method of the present invention	Same as above							Anode: 5
20	Method of the present invention	A							Cathode → Anode: 4
21	Not the method of the present invention	C							Anode: 5
22	Comparative method	A	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 50 seconds
23	Comparative method	B	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 40 seconds
24	Comparative method	C	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 40 seconds

25	Comparative method	A	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 70 seconds
26	Comparative method	B	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 60 seconds
27	Comparative method	C	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 60 seconds

A: 430-group

B: 410-group

C: 409-group

D: 7 % Cr-containing steel

(All were the annealed material with a plate thickness of 1.0 mm)

Cathode: cathode electrolysis

Anode: anode electrolysis

[Translator's note: numbers are omitted.]

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Table 1: Working Examples of the present invention: No. 1 (continued from above)

Test No.	External appearance		Contact resistance (mΩ)	Corrosion resistance*	Remark
	Visual evaluation	GDS*			
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14	Excessive acid				

	pickling				
15					
16					
17					
18					After the 0.5 % skin pass, acid pickling
19					After the shot blasting, acid pickling
20					
21					
22					
23					
24					
25					
26					
27					

*: Measurement of the oxide film by glow discharge. *: SST 96llrs pursuant to JIS Z-2371

1: Complete removal of the oxide film <--> 10: Non-acid pickling state

◎ : Good <--> X: Poor

[Translator's note: numbers and marks (◎, Δ & X) are omitted.]

Amendment

March 7, 1986

To: Mr. Michiro Uga, Commissioner of Patents

1. Disclosure of the Case

Japanese Patent Application No. Sho 60-115274

2. Title of the Invention

Method of Acid Pickling of Cr-containing Steel Plate

3. Party who makes the Amendment

Relationship with the case: Patent Applicant
Address: 2-6-3 Ohtemachi, Chiyoda-ku, Tokyo
Name: (665) Nippon Steel Co., Ltd.
Representative: Yutaka, Takeda

3. Agent

Address: T105, 8th Floor, Mori Building No. 1, 1-12-1
Nishi-shinbashi, Minato-ku, Tokyo, Tel: (503)4877
Name: Patent Attorney (6496): Yasushi, Yoshijima

4. Date of Amendment Directive

Voluntary

6. Subject of the Amendment

Entire specification and drawings

7. Content of the Amendment

The specification is amended as the Attachment.

Figures 1 (a), (b) and (c) are added as the Attachment.

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SPECIFICATION

1. Title of the Invention

METHOD OF ACID PICKLING OF CR-CONTAINING STEEL PLATE

2. Scope of Patent Claims:

(1) A method of acid pickling of a Cr-containing steel plate, characterized in that a Cr-containing steel plate, which is coated with an oxide film, is electrolytically pickled in a pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein fluorosilicate salt and fluoroborate salt are mixed and then one type or two or more types of nitrate salt and sulfate salt are mixed.

3. Detailed Description of the Invention

[Technical Application Field of the Invention]

The present invention relates to a method of acid pickling of a Cr-containing steel plate such as an alloy steel plate containing a small amount of Cr, austenite group steel plate, ferrite group steel plate, martensite steel plate and stainless steel plate.

[Prior Art]

The oxide film, which is generated on the surface of a steel plate containing a small amount of Cr, which has heat history of hot rolling or heat stretching/annealing, or a Cr-alloy steel plate, which is annealed after being cold-rolled, causes many problems such as damaging of the flat and smooth surface of the

finished product and shortening of the life of the dice, which is used during the spinning process. Therefore, it is necessary to completely remove said oxide film. To achieve this purpose, various types of acid pickling solutions are used. For example, as examples of the above described acid pickling solutions, "Steel Handbook by Maruzen KK, page 1258, table 15.3 (April 5, 1962)" discloses a solution of nitric acid and boric acid, solution of sulfuric acid, boric acid and chromic acid and solution of sulfuric acid, nitric acid and boric acid. In addition, Japanese unexamined published application No. Sho 56-81688 discloses a sulfuric acid solution and a mixed solution of ferric sulfate and sulfuric acid as the acid pickling solutions.

[Problem to be Solved by the Invention]

By using one of the above described acid pickling solutions, it is possible to effectively perform the acid pickling in the dipping process. To complete the acid pickling in a shorter period, it is necessary to use the electrolytic method. If the above described acid pickling solution is used, it is possible to remove the oxide film in a relatively short period and the finished surface has a fairly good appearance. However, the rate of deterioration of the performance of the solution is significantly fast and the cost of the acid pickling is increased. Especially, when the acid pickling solution, which is mainly made

from nitric acid and boric acid, is used in a long acid pickling/dipping process, the finished surface of the steel plate tends to significantly deteriorate.

As another method of removing the oxide film, it is possible to use the method wherein the oxide film is electrolyzed in a neutral salt aqueous solution such as sulfate of soda. In this case, however, iron in the steel plate is rarely dissolved and, although the finished surface is macroscopically good, microscopic oxide films tend to remain, or the Cr-deficient debris remains thereby deteriorating the corrosion resistance. Therefore, it is necessary to apply the method for a long period of time.

In addition, as the method of treating salt, it is possible to use the method wherein the oxide film is treated in mixed molten salt of caustic soda, caustic potash and nitrate of soda and then electrolyzed in a nitrate aqueous solution. However, the cost of this method is high.

The objective of the present invention is to solve the above described problems of the conventional acid pickling technologies and provide the method of acid pickling of a Cr-containing steel plate, wherein the steel plate with a good finished surface can be obtained by a short-period electrolytic treatment.

[Means Used to Solve the Problem]

The present invention solves the problems of the method of acid pickling of a Cr-containing steel plate by electrolytic pickling the Cr-containing steel plate, which is coated with an oxide film, in a pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein fluorosilicate salt and fluoroborate salt are mixed and then one type or two or more types of nitrate salt and sulfate salt are mixed.

[Operation]

Next, the detail of the present invention will be described.

A steel plate containing a small amount of Cr, which has heat history of hot rolling or heat stretching/annealing, or a Cr-containing steel plate such as a stainless steel plate, that is, the steel plate wherein an oxide film with a large thickness, which damages various practical properties, is coated on the surface, is electrolytically pickled in an acid pickling solution, which is made from 20 to 400 g/l of sulfuric acid aqueous solution wherein fluorosilicate salt and fluoroborate salt are mandatorily mixed as the acid pickling speed promoting agents and then one type or two or more types of nitrate salt and sulfate salt are selectively mixed.

According to the present invention, sulfuric acid, which is used as the base compound, is added to the solution so as to increase the lytic action and conductivity of the oxide film.

When sulfuric acid is used together with other solvents, which are used in the present invention, if its concentration is less than 20 g/l, the acid pickling efficiency is significantly decreased. If the concentration of sulfuric acid is more than 400 g/l, the acid pickling is excessive thereby damaging the surface and thus the external appearance. Therefore, according to the present invention, sulfuric acid is used at the concentration of 20 to 400 g/l.

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Fluorosilicate salt such as fluorosilicate of soda and potassium fluorosilicate and fluoroborate salt such as fluoroborate of soda and ammonium fluoroborate, which are mandatorily mixed in the sulfuric acid aqueous solution, can significantly increase the speed of removing the oxide film.

Figures 1 (a) to (c) show the effect of removing the oxide film of Na_2SiF_6 in a H_2OSO_4 - Na_2SiF_6 - NaNO_3 - Na_2SO_4 -group acid pickling solution.

(Condition)

(1) Solution:

Na_2SO_4 : 100 g/l

Na_2SiF_6 : various types

NaNO_3 : 100 g/l

H_2OSO_4 : 100 g/l

(2) Temperature: 60 °C

(3) Period: 1 to 10 sec.

(4) Current density: 60 A/dm²

The original plates, which were acid pickled, were:

(13 Cr, oxide film: 0.1 μ)

(13 Cr, oxide film: 0.2 μ)

(18 Cr, oxide film: 0.1 μ).

Although the degree of manifestation of the effect varies depending on the characteristics of each of the original plates, which were acid pickled (elements and thickness of the oxide film, etc.), it is obvious that, by adding 0.5 g/l or more of Na₂SiF₆, the acid pickling speed was significantly increased.

In addition, nitrate salt, which is selectively mixed in the solution, not only improves the speed of removing the oxide film, but also has the effect of inhibiting the excessive acid pickling of the base. Although sodium nitrate is most commonly used as nitrate salt, any nitrate salt such as potassium nitrate and ammonium nitrate can be effectively used.

Sulfate salt such as sodium sulfate has the effect of inhibiting the excessive electrolytic acid pickling. This effect is especially conspicuous in the Cr-alloy steel plate, which contains a relatively small amount of Cr.

Various types of the above described additives must be selectively used depending on the type of the subject steel and the thickness of the oxide film, which is determined by the

manufacturing process. Basically, as the content of Cr is increased, the temperature, to which the steel is exposed during the manufacturing process, is increased and the period of the treatment is increased, the number and concentration of the additives are increased.

As for the polarity of the electrolytic acid pickling, according to the present invention, normally, the steel plate is used as the anode. Depending on the type of the steel and the intended-end usage, first the cathode is acid pickled for a short period and subsequently the anode is acid pickled. The order of acid pickling is discretionally selected. In addition, when the thickness of the oxide film is extremely large or the oxide film must be removed in a significantly short period, a mechanical treatment such as the pre-acid pickling skin pass process, repeated bending process and shot blasting process can facilitate removal of the oxide film.

[Working Example 1]

430-group, 410-group and 409-group stainless steel plates and a cold-rolled 7 % Cr-containing steel plates were annealed in a continuous annealing line thereby removing the oxide films under the acid pickling conditions shown in Table 1. As shown in Table 1, the Cr-containing steel plates, which were acid pickled under the conditions of the present invention, had excellent performance in the external appearance, contact

resistance and corrosion resistance, which matched that of the conventional method, which requires the long-period treatment.

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Table 1: Working Examples of the present invention: No. 1

Test No.	Subject	Original plate	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)
			H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆			
1	Not the method of the present invention	A								Anode: 10
2	Method of the present invention	A								Anode: 7
3	Method of the present invention	C								Anode: 6
4	Method of the present invention	A								Anode: 6
5	Method of the present invention	B								Anode: 5
6	Method of the present invention	C								Anode: 3
7	Method of the present invention	A								Anode: 5
8	Method of the present invention	A								Anode: 5
9	Method of the present invention	D								Anode: 7
10	Method of the present invention	A								Anode: 10
11	Method of the present invention	A								Anode: 5
12	Method of the present invention	B								Anode: 5

13	Method of the present invention	C							Anode: 5
14	Not the method of the present invention	A							Anode: 5
15	Method of the present invention	A							Anode: 5
16	Method of the present invention	B							Anode: 5
17	Method of the present invention	C							Anode: 5
18	Method of the present invention	A (Especially large thickness of the oxide film)							Anode: 5
19	Method of the present invention	Same as above							Anode: 5
20	Method of the present invention	A							Cathode → Anode: 4
21	Not the method of the present invention	C							Anode: 5
22	Comparative method	A	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 50 seconds
23	Comparative method	B	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 40 seconds
24	Comparative method	C	Molten salt dipping → HNO ₃ electrolysis (conventional method)						Treatment of total of 40 seconds

25	Comparative method	A	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 70 seconds
26	Comparative method	B	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 60 seconds
27	Comparative method	C	Neutral salt electrolysis → Nitrate dipping (conventional method)			Treatment of total of 60 seconds

A: 430-group

B: 410-group

C: 409-group

D: 7 % Cr-containing steel

(All were the annealed material with a plate thickness of 1.0 mm)

Cathode: cathode electrolysis

Anode: anode electrolysis

[Translator's note: numbers are omitted.]

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Table 1: Working Examples of the present invention: No. 1 (continued from above)

Test No.	External appearance		Contact resistance (mΩ)	Corrosion resistance*	Remark
	Visual evaluation	GDS*			
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14	Excessive acid				

	pickling				
15					
16					
17					
18					After the 0.5 % skin pass, acid pickling
19					After the shot blasting, acid pickling
20					
21					
22					
23					
24					
25					
26					
27					

*: Measurement of the oxide film by glow discharge. *: SST 96llrs pursuant to JIS Z-2371

1: Complete removal of the oxide film <--> 10: Non-acid pickling state

◎ : Good <--> X: Poor

[Translator's note: numbers and marks (◎, Δ & X) are omitted.]

[Working Example 2]

In addition, the method of the present invention can be effectively used to remove the oxide film, which has an extremely large thickness, from the Cr alloy steel plate such a hot-rolled plate. The method of the present invention can be used singly or in combination with the conventional dipping acid pickling method. Table 2 shows examples of removal of the oxide films.

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Table 2: Working Examples of the present invention: No. 2

No.	Original plate (hot-rolled plate)	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)	Oxide film removal rate (%)	Remark
		H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆					
i	A										
ii	B										
iii	C										
iv	D								90 seconds dipping		Comparative Example
v	E										

A: 430-group

B: 410-group

C: 409-group

*Measurement by
GDS

[Translator's note: numbers are omitted.]

[Working Example 3]

In addition, the method of the present invention is effective in removing the oxide film from the Cr-containing steel plate, which is annealed at 800 to 1,000 °C for 1 minute after being hot-rolled. The method of the present invention can be used singly or in combination with the conventional dipping acid pickling method. Table 3 shows examples of removal of the oxide films.

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Table 3: Working Examples of the present invention: No. 3

No.	Original plate (hot-rolled and annealed plate)	Composition of the acid pickling solution (g/l)					Temperature °C	Current density A/dm ²	Period of electrolysis (sec)	Oxide film removal rate (%)	Remark
		H ₂ SO ₄	NaNO ₃	NaS ₄	Na ₂ SiF ₆	NaBF ₆					
I	A										
II	B										
III	C										
IV	D								120 seconds dipping		Comparative Example
V	E										

A: 430-group

B: 410-group

C: 409-group

*Measurement by GDS

[Translator's note: numbers are omitted.]

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[Effect of the Invention]

As described above, the present invention provides the method of rapidly acid pickling the oxide film, which can decrease the cost of the high-speed mass production of the Cr-containing steel plates. The method of the present invention is excellent in economic efficiency and prevention of the pollution and has a significantly high industrial value.

4. Brief Description of the Drawings

Figures 1 (a), (b) and (c) show the effect of removing the oxide film of Na_2SiF_6 in a H_2OSO_4 - Na_2SiF_6 - NaNO_3 - Na_2SO_4 -group acid pickling solution.

[Figure 1]

(a)

(x-coordinate)

External appearance 1

(y-coordinate)

Period of electrolysis (sec)

13 Cr, oxide film 0.1 μ

(b)

(x-coordinate)

External appearance 1

(y-coordinate)

Period of electrolysis (sec)

13 Cr, oxide film 0.2 μ

(c)

(x-coordinate)

External appearance 1

(y-coordinate)

Period of electrolysis (sec)

18 Cr, oxide film 0.1 μ

-- Not added
-- 0.25 g/l
-- 0.5
-- 1.0
-- 3.0
-- 5.0
-- 10.0
-- 15.0

⊙: Oxide film was completely removed.

○: A small amount of the oxide film remained.

△: A significant amount of the oxide film remained.

X: Almost no oxide film was removed.